

MINEROLOGIC & PETROLOGIC STUDIES OF METEORITES
AND LUNAR SAMPLES

GRANT NAG5-4617

FINAL REPORT

For the period 1 February 1997 through 31 March 2000

Principal Investigator

Dr. John Wood

June 2000

Prepared for

National Aeronautics and Space Administration

Washington, D.C.

Smithsonian Institution
Astrophysical Observatory
Cambridge, Massachusetts 02138

The Smithsonian Astrophysical Observatory
is a member of
Harvard-Smithsonian Center for Astrophysics

The NASA Technical Officer for this grant is
Dr. J. Boyce, NASA Headquarters, Code SR
Washington, D.C. 20546

Science/Technical/Management section

1. FINAL REPORT, NAG5-4617

New publications and MSS. submitted (May 20, 1999-May 16, 2000)

- [1] Petaev M. I. and Wood J. A. (2000) The condensation origin of zoned metal grains in Bencubbin/CH – like chondrites: Thermodynamic model. *Lunar Planet. Sci.* **31**, Abstract # 1608, Lunar and Planetary Institute, Houston (CD-ROM).
- [2] Meibom A., Petaev M. I., Krot A. N., Wood J. A., and Keil K. (1999) Primitive FeNi metal grains in CH carbonaceous chondrites formed by condensation from a gas of solar composition. *J. Geophys. Res.-Planets* **104**, 22053-22059.
- [3] Meibom A., Krot A. N., Petaev M. I. and 12 others (1999) Metal condensates in CH and Bencubbin-like chondrites: Evidence for localized nebula heating events and variations in gas composition (abstract). *Meteorit. & Planet. Sci.* **34**, A80-A81.
- [4] Meibom A., Desch S.J., Krot A. N., Cuzzi J. N., Petaev M. I., Wilson L., and Keil K. (2000) Large scale thermal events in the solar nebula recorded in chemically zoned Fe,Ni metal condensates in CH carbonaceous chondrites. *Lunar Planet. Sci.* **31**, Abstract #1477, Lunar and Planetary Institute, Houston (CD-ROM).
- [5] Meibom A., Desch S.J., Krot A. N., Cuzzi J. N., Petaev M. I., Wilson L., and Keil K. (2000) Large scale thermal events in the solar nebula recorded in chemically zoned Fe,Ni metal condensates in CH carbonaceous chondrites. *Science* **288**, 839-841.
- [6] Petaev M. I., Meibom A., Krot A. N., Wood J. A., Keil K. (2000) The condensation origin of zoned metal grains in QUE94411: Implications for the formation of Bencubbin/CH – like chondrites. *Lunar Planet. Sci.* **31**, Abstract # 1606, Lunar and Planetary Institute, Houston (CD-ROM).
- *[7] Petaev M. I., Meibom A., Krot A. N., Wood J. A., Keil K. (2000) The condensation origin of zoned metal grains in QUE94411: Implications for the formation of the Bencubbin/CH – like chondrites. *Meteorit. & Planet. Sci.*, submitted
- [8] Krot A. N., Sahijpal S., McKeegan K. D., Weber D., Ulyanov A. A., Petaev M. I., Meibom A. and Keil K. (1999) Unique mineralogy and isotopic signatures of Ca-Al-rich inclusions from the CH chondrite Acfer 182 (abstract). *Meteorit. & Planet. Sci.* **34**, A69-A70.
- [10] Krot A. N., Meibom A., Petaev M. I., Keil K., Zolensky M. E., Saito A., Mikai M., Ohsumi K. (2000) Ferrous silicate spherules with euhedral Fe,Ni-metal grains in CH carbonaceous chondrites: Evidence for condensation under highly oxidizing conditions. *Lunar Planet. Sci.* **31**, Abstract #1459, Lunar and Planetary Institute, Houston (CD-ROM).
- [11] Krot A. N., Meibom A., Petaev M. I., Keil K., Zolensky M. E., Saito A., Mikai M., Ohsumi K. (2000) Ferrous silicate spherules with euhedral Fe,Ni-metal grains in CH carbonaceous chondrites: Evidence for condensation under highly oxidizing conditions. *Meteorit. & Planet. Sci.*, submitted
- [12] Krot A. N., Weisberg M. K., Petaev M. I., Keil K., Scott E. R. D. (2000) High-temperature condensation signatures in Type I chondrules from CR carbonaceous chondrites. *Lunar Planet. Sci.* **31**, Abstract #1470, Lunar and Planetary Institute, Houston (CD-ROM).
- [13] Krot A. N., Hiaygon H., Petaev M. I., Meibom A. (2000) Oxygen isotopic compositions of secondary Ca-Fe-rich silicates from the Allende dark inclusion: Evidence against high-temperature formation. *Lunar Planet. Sci.* **31**, Abstract # 1463, Lunar and Planetary Institute, Houston (CD-ROM).
- [14] Krot A. N., Petaev M. I., Meibom A., and Keil K. (2000) In situ growth of Ca-rich rims around Allende dark inclusions. *Geochemistry International, Spec. Issue*, accepted.
- [15] Krot A. N., Petaev M. I., Brearley A. J., Kallemeyn G. W., Sears D. W. G., Benoit P. H., Hutcheon I. D., and Keil K. (1999) In situ growth of fayalite and hedenbergite in the ungrouped carbonaceous chondrite MacAlpine Hills 88107 (abstract). *Meteorit. & Planet. Sci.* **34**, A68.
- [16] Krot A. N., Brearley A. J., Petaev M. I., Kallemeyn G. W., Sears D. W. G., Benoit P. H., Hutcheon I. D., Zolensky M. E., and Keil K. (2000) Evidence for in situ growth of fayalite and hedenbergite in MacAlpine

- 88107, ungrouped carbonaceous chondrite related to CM-CO clan. *Meteorit. & Planet. Sci.*, submitted.
- [17] Krot A. N., Petaev M. I., Bland P., Todd C. S., Keil K. (2000) Metal-sulfide-Fe,Ni-carbide-fayalite assemblages in the reduced CV chondrite breccia Vigarano. *Meteorit. & Planet. Sci.*, submitted.
- [18] Petaev M. I., Clarke R. S., Jarosewich E., Zaslavskaya N. I., Kononkova N. N., Wang M.-S., Lipschutz M. E., Olsen E. J., Davis A. M., Steele I. M., Clayton R. N., Mayeda T. K., Wasson J. T. (2000) The Chaunskij anomalous mesosiderite: Petrology, chemistry, oxygen isotopes, classification and origin. *Geochemistry International, Spec. Issue*, accepted.
- [19] Yin Q. Z., Jacobsen S. B., McDonough W. F., Horn I., Petaev M. I., Zipfel J. (2000) The $^{92}\text{Nb} - ^{92}\text{Zr}$ *p*-Process Chronometer. *Astrophys. J.*, in press
- [20] Wood, J. A. (2000) The beginning: Swift and violent. *Space Sci. Rev.*, in press, and in *Dust to Terrestrial Planets* (Kluwer Academic Publ., Dordrecht), in press.
- [21] Wood, J. A. (2000) Pressure and temperature profiles in the solar nebula. *Space Sci. Rev.*, in press, and in *Dust to Terrestrial Planets* (Kluwer Academic Publ., Dordrecht), in press.

*Copies appended.

Introduction

In the past year this group continued essentially full time research on extraterrestrial materials, and the question of the origin of the solar system. The continuing scientific staff consists of the P.I. and Visiting Scientist Michael Petaev. *Vitae* for Wood and Petaev appear in Sec. 6. We benefit from the part time services of a Project Administrator (Judith Terry) and a Secretary (Muazzez Lohmiller).

In January 1999 the P.I. assumed the Chairmanship of COMPLEX, the Committee on Planetary and Lunar Exploration of the Space Studies Board, National Research Council.

Wood and Petaev were authors or coauthors of 21 publications, new manuscripts, and abstracts in the last year. These are listed above, and referenced by number [*n*] in the discussion below. Other references to the literature made in this Section are listed in Sec. 3.

New PCMET and CWPI condensation codes

Two new Fortran codes – PCMET (for Co-bearing systems) and CWPI (for Mn-bearing systems) – have been developed from our previous codes PHEQ (Wood and Hashimoto, 1993) and PHEQ4 (Petaev and Wood, 1998a) which model nebular condensation in the H-C-O-Na-Mg-Al-Si-S-Ca-Fe and H-C-N-O-Na-Mg-Al-Si-P-S-Cl-K-Ca-Ti-Cr-Mn(Co)-Fe-Ni systems, respectively. Both codes implement the CWPI condensation model (Petaev and Wood, 1998), which allows for programmed withdrawal of minerals that are no longer accessible to reaction as they condense. Solid solution models and the thermodynamic database were substantially modified to resolve inconsistencies reported in our previous work (Petaev and Wood, 1998b). The new solid solution models that have been added are as follows: corundum ($\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$), olivine ($\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4 - \text{CaMgSiO}_4 - \text{CaFeSiO}_4 - \text{Ni}_2\text{SiO}_4$), orthopyroxene ($\text{Mg}_2\text{Si}_2\text{O}_6 - \text{Fe}_2\text{Si}_2\text{O}_6$), melilite ($\text{Ca}_2\text{Al}_2\text{SiO}_7 - \text{Ca}_2\text{MgSi}_2\text{O}_7$), plagioclase ($\text{CaAl}_2\text{Si}_2\text{O}_8 - \text{NaAlSi}_3\text{O}_8 - \text{KAlSi}_3\text{O}_8$), clinopyroxene ($\text{CaMgSi}_2\text{O}_6 - \text{CaAl}_2\text{SiO}_6 - \text{CaTi}_{0.5}\text{Mg}_{0.5}\text{AlSiO}_6$), metal (Fe – Ni – Co – Si – Cr, Co ideal), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} - \text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), and spinel ($\text{MgAl}_2\text{O}_4 - \text{FeAl}_2\text{O}_4 - \text{FeCr}_2\text{O}_4 - \text{MgCr}_2\text{O}_4$). Sources of thermodynamic data are listed in [1].

To test our codes we compare our condensation sequence calculated for a nebula of solar composition (Anders and Grevesse, 1989) at $P_{\text{tot}}=10^{-3}$ bar with that of Yoneda and Grossman (1995) [YG95], in Table 1. It should be noted that our database of condensed phases is ~5 times larger than that of [YG95]. Our condensation sequence includes all the phases of [YG95] plus $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, $\text{Ca}_3\text{Ti}_2\text{O}_7$, barringerite, and schreibersite, which were not included in their database. In order to

Table 1. Condensation temperatures (°K) of phases stable in a system of solar composition at $P_{\text{tot}}=10^{-3}$ bar.

Mineral	This study		[YG95]	
	In	Out	In	Out
Corundum	1777	1700	1770	1740
Hibonite	1770	1495	1743	1500
Corundum	1599	1498		
Perovskite	1696	1460	1688	1448
Grossite	1660	1592		
Melilite ss	1629	1426	1625	1444
Spinel	1500	1416	1501	1409
Metal ss	1475		1464	
Cpx ss	1472		1449	
Olivine ss	1452		1443	
Pl ss	1444		1416	
Ti ₃ O ₅	1381	1275	1386	1361
Opx ss	1377		1366	
Ti ₄ O ₇	1360	1185	1361	
Cr-spinel ss	1212		1221	
Rutile	1185			
Sphene	1094		1217	

due to the ideal solid solution model of clinopyroxene used by [YG95]. Moreover, our composition of Ti, Al-rich clinopyroxene is fully consistent with the compositional zoning in the clinopyroxene in Fluffy Type A CAIs (e.g., Brearley and Jones, 1998) which are considered to be nebular condensates. The greater stability of clinopyroxene in our database is unquestionably responsible for the large difference in condensation temperatures of sphene in Table 1. The difference in plagioclase condensation temperatures is probably caused by differences in the solid solution models. There are also substantial differences in the stability fields of hibonite and grossite between [YG95] and our work, which result from differences in thermodynamic data used for these minerals. We prefer the more precise data of Kumar and Kay (1985) which predict stability fields of hibonite and grossite that are consistent with the earlier calculations of Kornacki and Fegley (1984).

The PCMET/CWPI code, run on a Windows NT-based PC (333 MHz processor, 64 MB RAM) typically needs 20-30 sec to calculate an equilibrium mineral assemblage. At the 31st LPSC we made our source codes and databases available to any interested party.

Thermodynamic model of condensation of Bencubbin/CH-like chondrite metal

Our earlier work on modeling condensation of CH chondrite metal [2-5] has been extended to Bencubbin/CH-like chondrites (QUE94411 and HH237), which are petrographically and chemically similar to CH chondrites but have higher metal abundances and contain more (15-20 vol. %) large zoned metal grains (Weisberg et al., 1999; Krot et al., 2000). Compositional profiles across eight large zoned metal grains of the QUE94411 were measured by our collaborators A. Meibom and A. N. Krot at the University of Hawaii. The profiles (see appended manuscript) show Ni concentrations gradually decreasing from cores of the grains to their rims. Co generally follows Ni, but many profiles are somewhat ragged. Most Cr profiles show fairly uniform Cr concentrations in the cores with gradual increase in the peripheral portions of the grains. In order to reproduce the compositional profiles in these grains we carried out detailed modeling of non-equilibrium metal condensation in nebular systems with non-solar dust/gas ratios [6,7] using our new PCMET code [1]. Calculations were made at a nebular pressure of 10^{-4} bar and for several sets of three parameters - Cr depletion factor, isolation degree ξ , and system dust/gas ratio - which were estimated from the

mineralogy and chemistry of the QUE94411 and HH237 chondrites. Details of our model are described in the appended manuscript [7].

It was found that the condensation of these grains took place under conditions that differed for each grain, indicative of a high degree of heterogeneity in the formation region of Bencubbin/CH-like chondrites. The relatively high ξ values (0.3–5 rel.% per K of cooling) required for condensation of these grains are attributable to non-equilibrium condensation resulting from rapid growth of the zoned metal grains. It was shown that the raggedness of the Co zoning profiles is apparently due to the growth of grain cores by coagulation of small, compositionally diverse grains of early Ni,Co-rich condensate rather than by direct deposition of Fe, Ni, Co, and Cr from the cooling nebular gas. The smooth compositional zoning of all elements in the grain rims is consistent with their direct deposition of Fe, Ni, Co, and Cr from the cooling nebular gas onto grain cores. Finally, zoned metal grains of the Bencubbin/CH-like chondrites must have been transported from their formation regions in order to escape secondary low-temperature alteration.

CR clan chondritic materials: Further support for the CWPI-type condensation

The recently recognized CR clan of meteorites includes the CR, CH, and Bencubbin/CH-like chondrites and the Acfer 182 and LEW 85332 ungrouped chondrites (Weisberg et al., 1995; Weisberg et al. 1999, Krot et al., 2000). These meteorites are quite different petrographically, but their similar mineralogical, chemical, and isotopic characteristics imply that they must have formed in the same nebular region from closely related reservoirs (Weisberg et al., 1995). Except for the original CR chondrites, other members of the CR chondritic clan have largely escaped secondary alteration, so they provide valuable information on the physicochemical conditions in their nebular source regions. During the last year we continued collaborative studies of these meteorites.

The CH chondrites contain a population of small (15–30 μm) ferrous silicate spherules which consist of cryptocrystalline ol-opx-normative material, SiO_2 -rich glass, and rounded-to-euhedral FeNi metal grains. The silicate portions of the spherules are highly depleted in refractory lithophiles (Ca, Al,Ti) and enriched in SiO_2 , FeO, MnO, Cr_2O_3 , and Na_2O relative to the dominant magnesian chondrules of the CH chondrites. The Fe/(Fe+Mg) ratios in silicates show strong positive correlation with Fe concentrations in coexisting metal grains, implying that this correlation is not due to a redox exchange of Fe between silicate melt and metal but is instead a nebular feature. We used our PCMET [1] and METEOMOD (Ariskin et al., 1997) thermodynamic codes to model the nebular condensation of solid precursor materials of these spherules, and their subsequent melting in a chondrule-forming event. Metal liquidus temperatures were calculated from an assessment of experimental data on the Fe-Ni system (Lee, 1993). It was found [10,11] that the observed properties of these spherules can be explained by non-equilibrium condensation of solid metal and silicate precursors in dust-enriched nebular systems (up to 300 \times solar) at 10^{-4} bar, followed by remelting of the precursor at relatively high f_{O_2} (2.1–3.1 log units below IW buffer) and crystallization of metal from supercooled (13–111 $^\circ\text{K}$) silicate melts.

Many Mg-rich porphyritic chondrules (Type I) of the CR chondrites are surrounded by SiO_2 -rich igneous rims which consist of chemically zoned Mn- and Cr-rich pyroxenes, glassy mesostases, rounded FeNi metal blebs, and a silica phase. The mesostases are enriched in Na and K and depleted in Ca relative to those of the host chondrules. [12] concluded that the chemical fractionations among precursor materials of the host chondrules and their rims were produced by isolation and subsequent melting of earlier, high temperature condensates in the course of nebular condensation in the formation region of CR chondrites, in accordance with condensation sequences predicted by the CWPI condensation model of Petaev and Wood (1998a).

Secondary alteration in carbonaceous chondrites

Petaev continued collaboration with the Hawaii group in studies of aqueous alteration in carbonaceous chondrites, which resulted in series of publications [13-16]. He carried out detailed thermodynamic analysis of the stability of the metal-sulfide-magnetite-Fe,Ni-carbide-fayalite assemblages observed by his collaborators in the reduced CV chondrite breccia Vigarano. It was found that carbidization of the metal might have taken place in either a nebular or an asteroidal environment (in the absence of liquid water). However, the observed subsequent replacement of altered magnetite-carbide-sulfide nodules by fayalite could have taken place only in the presence of an aqueous solution, in an asteroidal environment at temperatures below $\sim 200^{\circ}\text{C}$. A major paper has been submitted for publication [17].

Silica nodules in Ca,Al-rich chondrules of the Kainsaz CO3 chondrite

In searching for Ca,Al-rich objects in the Kainsaz CO3 chondrite, a variety of chondrules and chondrule fragments with high abundance of plagioclase as well as numerous CAIs were identified in detailed X-ray maps of 3 thin sections. Among numerous An-rich chondrules with crystalline, silica-bearing mesostases, two chondrules (Fig. 1) contain unusual SiO_2 -rich nodules texturally reminiscent of immiscible silicate melts.

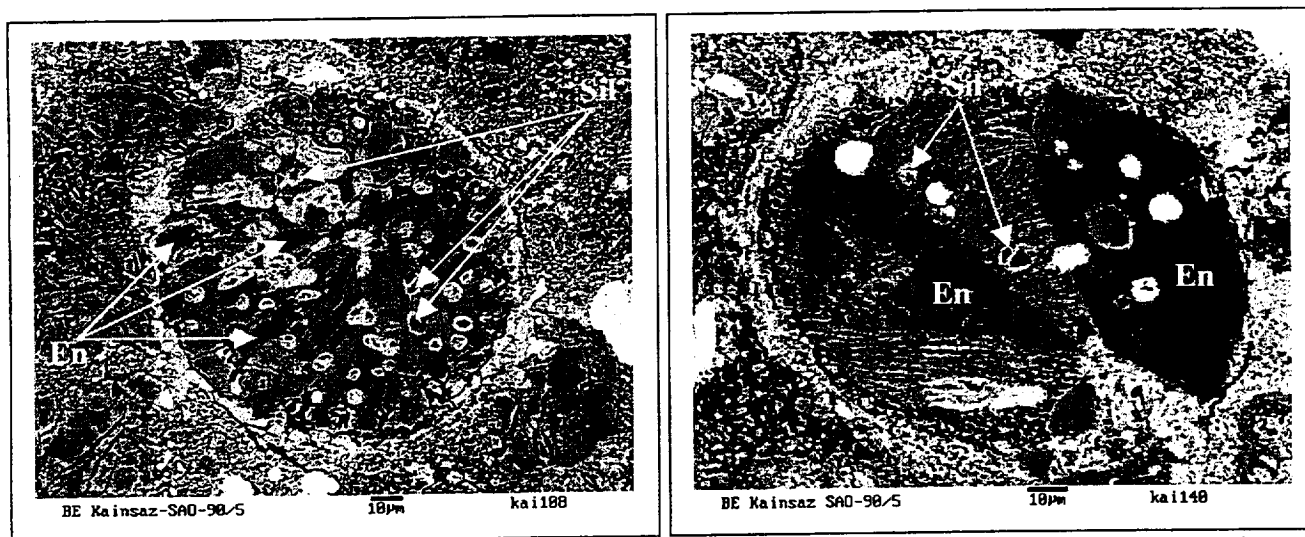


Fig. 1. SiO_2 -bearing chondrules in the Kainsaz CO3 chondrite. White – opaque minerals, light gray – hedenbergite, medium gray – augite, dark gray – enstatite (En) and mesostasis, dark – a silica phase (Sil), black – voids.

Only one of these chondrules (left panel in Fig. 1) has been studied in detail as yet. It consists of large subhedral grains of enstatite (20.5 vol. %) and Al,Cr-bearing augite (28.6 %) enclosed in plagioclase-rich mesostasis (25.8 %). Numerous nodules (24.4 %) of almost pure SiO_2 and secondary hedenbergite are enclosed in all phases but enstatite. Many hedenbergite nodules contain tiny relic grains of SiO_2 , unambiguous evidence for the substitution of hedenbergite for a silica mineral, probably in an asteroidal environment. An unusually SiO_2 -rich bulk chemical composition of the chondrule (67 wt. % SiO_2 , 5.3 % Al_2O_3 , 1.6 % FeO , 16.5 % MgO , 6.5 % CaO , 0.9 % Na_2O) means that initial crystallization of enstatite further increased the SiO_2 content of the residual melt to as much as ~ 71 wt. % which is enough for a silica mineral to appear on the liquidus, but certainly not high enough for liquid immiscibility to occur in the CMAS system (Berman, 1983). It appears that enstatite and a silica phase crystallized before augite, which is consistent with the crystallization sequence inferred from petrographic observations, but this cannot explain the nodular appearance of the silica phase. High concentrations of Al_2O_3 , CaO , SiO_2 and Na_2O in the chondrule imply that the

chondrule precursors formed in a highly fractionated nebular system, depleted in Mg and Fe. Further study of these unusual chondrules is in progress.

Early solar system chronology

Recently we began a long-term collaborative program with the Department of Earth and Planetary Sciences at Harvard University (Prof. S. B. Jacobsen, Dr. Q. Z. Yin) to study early solar system chronology. Because the distribution of ^{26}Al and ^{53}Mn in the early solar system may have been inhomogeneous (e.g., Lugmair and Shukolyukov, 1998; Wood, 1998) we intend to study other extinct nuclide systems such as $^{92}\text{Nb} - ^{92}\text{Zr}$, $^{182}\text{Hf} - ^{182}\text{W}$, $^{97}\text{Tc} - ^{97}\text{Mo}$, $^{107}\text{Pd} - ^{107}\text{Ag}$.

Before using the $^{92}\text{Nb} - ^{92}\text{Zr}$ system for precise dating of early solar processes, the initial abundances of both isotopes need to be measured in samples of known age. One of the best minerals to use for measuring Zr isotopes is meteoritic zircon. Last year we searched for zircon grains by making fine-scale X-ray maps of 7 polished sections of the Chaunskij mesosiderite and several thin sections of the Bereba, Cachari, and Pasamonte eucrites. Given the rarity and very small grain size of meteoritic zircon, the search for them is extremely time consuming. Eucrites contain only tiny (1-2 μm) zircon grains, but in Chaunskij a large (~15 μm) euhedral zircon grain was found, in addition to another grain that we reported earlier [18]. Laser ablation ICP-MS measurements of Zr and Nb isotopes in one zircon grain from Chaunskij and several rutile grains from the Zagora and Toluca meteorites [19] revealed that the Chaunskij zircon is 64-97 Ma older than the rutile grains. The other zircon grain from Chaunskij has been saved for precise U-Pb study by the SHRIMP ion probe at Stanford University, which is in progress.

Wood reviewed isotopic evidence for the need to accrete planetesimals very early, while enough ^{26}Al remained alive so that its decay could provide the heat needed to metamorphose the OC parent bodies and, especially, to partially melt the eucrite parent body [20]. This short time scale of accretion is consistent with the early time of formation of chondrules and CAIs Wood (1996) has argued for, during which the large amounts of energy dissipated by disk accretion would be available for the thermal processing of those objects. Noting the dependence of meteoriticists on outdated estimates of pressure and temperature profiles in the solar nebula, such as that of Lewis (1972) (28 years old!) Wood [21] also reviewed modern astrophysical estimates of these parameters, noting that they changed very rapidly with early nebular evolutions and did not become quasi-stable until the quiescent disk phase, by which time P and T in the vicinity of the present asteroid belt were far too low to be consistent with chondrule and CAI formation.